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A CRITIQUE ON DISINFECTION OF DRINKING WATER

By

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Chapter 1

A LOOK BACK

The establishment of disinfection as a scientific process of killing germs in water was an outcome of two significant theories in the second half of the nineteenth century. The first of these theories, generally known as the germ theory of communicable diseases, was first presented in 1834 by Agostino Bassi. This was followed by Jacob Henle's formulation in 1840 which put forth the view that living microscopic organisms were the cause of contagious and infectious diseases. Unfortunately, for some time this theory could not be authenticated for lack of experimental and observational proofs. It was in 1876 that Robert Koch, one of Henle's students, conclusively proved to the scientific community the validity of Henle's theory (Rosen, 1958).

The second theory owes its origin to John Snow (1813-1858) who was a medical practitioner in London. He was a keen observer of cholera epidemic in London in 1831-32 and actively studied its recurrence in 1848. He published his observations in 1849 as a pamphlet entitled "On the Mode of Communication of Cholera." During the epidemic of 1854, his systematic investigations included the consumers of water from the Broad Street pump. This study published in another pamphlet showed that the number of deaths in each area corresponded to the degree of pollution of the part of the Thames River from which each company obtained its water. His definitive views on the spread of cholera can be summarized as follows:

i) The "poison" of cholera enters the alimentary canal directly by mouth, and this "poison" is probably a specific living being derived from the excreta of a cholera patient;

ii) Cholera can be transmitted from person to person through soiling of the hands or through contaminated food and water;

iii) In case of Broad Street pump water users, a damaged sewer made it possible for the dangerous wastes from cholera patients to permeate the ground and pollute wells or other supplies of water used by the community.

Perhaps his most significant conclusion was that the cholera "poison" could be carried in water. However, he could not identify the infective agent. Snow's theory was supported by the establishment of the germ theory. However, it was substantiated only when Koch isolated and cultivated *Vibrio cholerae* in 1883. Thus began an important era in the history of public health which could be termed as the birth of modern sanitary engineering.

From the history of the theory of spread of disease or infection, the term "disinfection" as now applied to "the destruction of water-borne pathogens" is probably very apt (Fair 1968). It is obvious, therefore, that "sterilization" (destruction of all living things in the medium sterilized.) must be distinguished from "disinfection."

The history of disinfection, at least its practice with or without intent, is as old as civilization. Baker (1948) cites others for reference to Sanskrit books in India wherein 'boiling', 'plunging hot metal into water', 'exposure to sunlight' and 'filteration through charcoal' were expressed as "useful practices." He also mentions Aristotle's (384-323 B.C.) advice to Alexander the Great wherein he says:

> "Do not let your men drink out of stagnant pools...And when you carry water on the desert marches it should first be boiled to prevent its getting sour."

The practice of boiling water appears to have been carried through Nero's reign (54-68 A.D.), Paulus Aegineta's time (a medical man of seventh century Greece) and Rhaze's period (an important Mohammedan physician of the ninth century A.D.). Boiling water prior to drinking was probably the only practice universal to all civilizations. It is still respected, though not practiced.

Among all the disinfectants which emerged during the bacteriological era following 1876, chlorine is the oldest and most widely used. In fact, until recently, chlorination was synonymous with disinfection. Sawyer (1967) points out that chlorination of water supplies on an emergency basis has been practiced since about 1850. Baker (1948) quotes Dr. Rohley Dunglinson in his "Human Health" (Philadelphia, 1835) to say that chlorine was proposed to be used to make "the waters of Marshes potable." In any case chlorination with a clear intent of disinfection of germs was adopted for public water supplies, though, on a limited scale, soon after the realization that water was a vehicle for many pathogenic germs. It is fortunate, however, that only a few of the numerous diseases which inflict man are water borne even though this number appears to be increasing with time owing to new discoveries. Table 1.1 shows the present situation with regard to many common diseases due to pathogenic bacteria and protozoa. The dates in this table are an indication of the rapid scientific progress following the statement of the germ theory. Tracing the history of disinfection further reveals how rapid were the efforts towards the annihilation of germ-causing diseases in many parts of the world. However, these efforts were highly controversial and generated severe opposition. Baker (1948) has

recorded an almost complete chronicle of how chlorination came to be accepted as a standard water disinfectant in the U.S. and elsewhere in the world. Twenty years of trials and tribulations here and there culminated in the famous court case regarding chlorination at the Boonton, New Jersey water treatment plant (1908). The decision upholding the right of the city to chlorinate the public water supply provided the impetus for the spread of chlorination for disinfection. The Boonton plant is reputed to be the first in the U.S.A. to employ a permanent chlorinating plant although the Bubbly Creek plant in Chicago started the practice of chlorination a few days earlier. However, the credit of being the first to establish a permanent chlorinating plant in the world goes to the water works at Middelkerke, Belgium (1902).

The practice of ozonation began about the same time as chlorination. However, chlorination became far more popular than ozonation in the U.S. Europeans, on the other hand, were more receptive to the use of ozone. It is still very popular there. Russia probably built the first ozonation plant in the world in 1905-6 at Tzarskoe Selo - Tzar's village (Faber, 1961) although a number of patents and papers relating to ozonation were issued between 1874 and 1905 in a number of countries. In the U.S.A. George A. Sopper, in the late 1890's, was the first engineer who recommended the use of ozone as a reliable disinfecting agent. The first ozonation tests were actually made in 1906 at an experimental filter plant at Jerome Park reservoir, New York City. That slight progress has been made by ozonation can be judged from the fact that only eight water works employed ozone during the period 1908-1942. Of these, five plants abandoned its use soon after. Comparative progress

of ozone in Europe can be seen from the fact that in 1940 there were 90 installations in France, 14 in Italy, 5 in Belgium, 4 in England, 3 in Romania and one in Russia.

Another agent that showed promise in the field of disinfection of water supplies was "ultraviolet rays." Baker found the earliest mention of its success as a disinfecting agent in 1877 which described its attempted use at Marseilles, France. The first known installation of ultraviolet ray apparatus in the U.S.A. was at Henderson, Kentucky in 1916, notes Baker. However, this method of disinfection of water never became popular in the U.S.A. and has not received any recognition even now. On the other hand Faber (1961) notes that this system is "widely in practice in the Soviet Union."

Faber (1961) found no known applications of bromine for the disinfection of drinking water supplies although it has good disinfecting ability and has been occasionally used for control of biological growths in industrial water supplies and swimming pools.

Chang (1966), relating the history of iodination of water supplies, gives credit to Vergnoux who reported on the first rapid sterilization of water for troops in 1915. Hinman and Hitchens, following this report, experimented with iodine and recommended its use in U.S.A. Iodine was later used by Dunham for disinfecting small water supplies in 1930 in the U. S.

By 1940 disinfection of drinking water by various physical and chemical means in general and by chlorine in particular, had achieved great popularity among the sanitary engineers and lot of practical knowledge about its application had been accumulated. But

TABLE 1.1

A. WATER-BORNE BACTERIAL DISEASES

No.	Disease	Germ	Year of Discovery	Investigator	Water-Borne
1.	Typhoid	*Salmonella typhi*	1880	Eberth	Yes
2.	Paratyphoid	*Salmonella paratyphi*	-	-	Yes
3.	Tuberculosis	*Mycobacterium tuberculosis*	1882	Koch	No
4.	Cholera	*Vibrio cholerae*	1883	Koch	Yes
5.	Diptheria	*Corynebacterium diphtheriae*	1884	Klebs & Loeffler	No
6.	Tetanus (Lockjaw)	*Clostridium tetani*	1884	Nicolaier	No
7.	Pneumonia	*Str. pneumoniae*	1886	Fraenkel	No
8.	Bacillary Dysentery	*Shigella dysenteriae*	1898	Shiga	Yes
9.	Plague	*Pasteurella pestis*	1894	Yersin, Kitasato	No

B. WATER-BORNE PROTOZOAN DISEASES

No.	Disease	Germ	Year of Discovery	Investigator	Water-Borne
1.	Amebic Dysentery	*Endamaeba histolytica*	-	-	Yes

very little was known about the fundamental chemistry of the disinfecting agents and the biology of the disinfecting action. Fortunately, during the early periods of the Second World War, in an effort to meet the urgent need for a suitable disinfecting agent for military use, particularly for the disinfection of canteen waters, a contract was awarded to Harvard University by the U.S. Army's Office of Scientific Research and Development (Committee on Medical Research) to make "studies and experimental investigations in connection with the disinfection of water and related substances." The final report of this contract which was executed by Fair (Responsible Investigator), Chang, Morris and many others, is an extensive study of almost all fundamental aspects of disinfection. Unfortunately the final report, as such, was never widely distributed due to its "restricted" classification. A portion of the findings did appear in a number of publications. In general this report dealt with the chemistry and biology involved in disinfections by chlorine, iodine and bromine.

In the following years of the Second World War, the attention of the sanitary engineer turned to another focal point in the area of disinfection. In the late forties and thereafter, remarkable discoveries were made in the field of virology. Faced by serious viral epidemics which were largely believed to be due to water-borne infectious hepatitis (Mosley, 1965), (see Appendix A for definition of term "water-borne"), the sanitary engineer was confronted by the twin problems of locating water-borne virus as well as their destruction. Much work has since been done but much more remains to be done. Table 1.2 lists various groups of virus which have been isolated from human feces. Some

of these are likely to be water-borne but this has yet to be proven in many cases (Berg 1964). So far only the virus of infectious hepatitis is accepted as water-borne (Mosley 1965).

The study of disinfection is still in its infancy. In fact, the great advances in the field of virology in recent years demand that sanitary engineers must make a reappraisal of prevailing disinfection practice. Disinfection problems promise to increase substantially in the near future due to greater reuse of water in the face of gross pollution in our surface waters. This review has been prepared as part of an effort to reawaken a wide interest in the field of water disinfection.

TABLE 1.2

VIRUSES OBTAINED FROM FECES*

No.	Disease	Associated Virus Group or Groups
1.	Paralytic Poliomyelitis	Poliovirus
2.	Aseptic Meningitis	Poliovirus, Coxsackie Virus A & Virus B, and Echovirus
3.	Pleurodynia	Coxsackie Virus B
4.	Herpangina	Coxsackie Virus A
5.	Respiratory	Echovirus, Adenovirus and Reovirus
6.	Enteritis	Echovirus, Reovirus
7.	Rash	Echovirus
8.	Acute Infantile Myocarditis	Coxsackie Virus B
9.	Jaundice	Infectious Hepatitis

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* This information is taken from "The Virus Hazard in Water Supplies" by G. Berg published in New England W. W. Association, 78:2:79 (June 1964). The listed viruses have been isolated from human feces and could be important in water supplies. However, infectious hepatitis is the only virus which has been conclusively proven to be water-borne.

Chapter 2

THE INFILTRATORS

2.1 Water-borne Pathogens

Water is disinfected in order to destroy those organisms which are water-borne and are pathogenic to man. Pathogens have been found to exist among the following groups of organisms:

A. Non-sporulating pathogenic enteric bacteria such as *Eberthela typhosa*, *Shigella dysenteriae* and *Vibrio comma*. An almost complete list of this type has been given in Table 1.1.

B. Pathogenic Protozoa - The cysts of *Endamoeba histolytica*, responsible for amebic dysentery, are probably the only water-borne pathogenic protozoa. Fair (1968) writes that other water-borne protozoa infections are "rare."

C. Pathogenic Worms - Among these worms, cercariae of schistosomes and cyclops are the most important.

D. Sporulating Bacterium - In this group, *Bacillus anthracis* is accepted as water-borne.

E. Virus - The feeling that water is a very important vehicle in the transmission of human viruses is growing. So far, infectious hepatitis is the only virus which is accepted as water-borne by epidemiologists. The question of whether the virus of poliomyelitis and other enterovirus are water-borne is still a matter of controversy.

2.2 Conventional Test Organism

The study of numerous non-sporulating pathogenic enteric

bacteria is often simplified by dealing with a non-pathogenic member of this group, Escherichia coli, an organism in human feces and generally somewhat more resistant to destruction than its pathogenic associates. (Harvard Report, 1945). This view has always been contested by some researchers (Kabler, 1951), (Baumann, 1961) but no other organism has been proven to be equally or more reliable. Almost all the research on disinfection done in the U.S. has involved either Escherichia coli or a specific pathogen.

Among the pathogenic protozoa cysts of Entamaeba histolytica, being more resistant, have always been adopted as test organisms for disinfection studies. However, the reported incidence of water-borne amebic dysentery is very low in the U.S. Their removal by filtration or sedimentation is extremely satisfactory (Fair et al. 1968, Morris 1966). As a result, this organism is not often considered as a test organism except in those cases where unfiltered water has to be disinfected or where the population of carriers of amebic cysts is large. Regarding its resistance to disinfectants, it is generally considered to be more resistant than E. coli (Morris 1966).

Pathogenic worms in general and cercariae of schistosomes in particular are not effectively removed by conventional water treatment methods (Harringer, 1949) and reliance has to be placed on disinfection. Fortunately, schistosomiasis or cercariae dermatitis is of rare occurrence in the U.S. (Fair et al. 1968) and thus there is little need to consider the worms as a test organism.

2.3 Challenge of Virus

The presence and survival of virus in water in general is no longer a controversial matter. Although infectious hepatitis is the only virus of human origin which has been conclusively proven to be water-borne, others have not been effectively disproved. (Mosley, 1965). Berg (1965), in the introduction to "Transmission of Viruses by the Water Route" poses the following questions on the status of virus in water supplies:

1. Is there inherent in this situation a danger, albeit inapparent, to those who must use this water for drinking purposes? That is, are small quantities of viruses present in our drinking water?
2. If they are, how can we detect them?
3. If we ingest them, how much virus is needed to produce an infection?
4. If small amounts of virus will produce infection, what proportion of those consuming such small amounts will become infected?
5. What viruses are important in water transmission?
6. To what extent are viruses of non-human origin important in human disease process?

While all these questions remain unanswered, the matter of immediate concern to the sanitary engineer is whether or not virus poses greater danger to man through water route than does pathogenic bacteria with the present minimum standards? Chang (1968) points out that "water polluted by sewage, sewage effluent, or the like is

apt to carry enteric viruses (and other pathogens), that flocculation, filtration, and marginal chlorination or ozonation (leaving very little or no residual) will probably not reduce the virus concentration to a safe level for mass consumption, and that the coliform index used as the minimum standard will not ensure the safety of the water against viral infections."* He further argues that only those viruses that grow in the intestinal wall of man and are discharged in large numbers in the feces deserve consideration. This criterion reduces them to the enteric group which comprises principally the enteroviruses (poliovirus, coxsackievirus and echovirus) and the virus of infectious hepatitis. Unfortunately the infectious hepatitis virus has been reported to be the most resistant of all virus in the entire group. It does not lend itself to laboratory examination or cultivation (Berg 1965, Chang 1968). Accordingly, the dependence has always been placed on poliovirus (Weidenkopf 1958), Coxsackie virus (Clarke et al. 1954) and adenovirus (Clarke, 1956) for experimental work. However, as Chang (1968) recommends, a slight margin of safety should be allowed on the assumption that the infectious hepatitis virus might be a little more resistant than the hardy enteroviruses.

2.4 Relative Concentrations of Organic Virus in Water and Sewage

Hoskins (1926) estimated that the number of coliforms dis-

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* "A viral infection means establishment of parasitism in a host by the virus, whereas, a virus disease is an infection with overt symptoms and signs" (Chang 1968).

charged by an individual daily is of the order of 400 billion. On this basis Fair et al. (Harvard Report, 1945) assumed that concentrated sewage may at times contain about 100 million coliform bacteria per 100 ml. Clarke (1962) reported that the mean coliform density in domestic sewage is 46×10^6 per 100 ml. But this high concentration may be present only in highly polluted waters. The density of <u>Esch</u>. <u>coli</u> in waters selected for public water supplies is probably a fraction of that in raw sewage. Streeter (1927) showed that the bacterial loading of a water supply prior to chlorination should desirably not exceed 50 <u>Esch</u>. <u>coli</u> per 100 ml if the treated water is to contain less than about one <u>Esch</u>. <u>coli</u> per 100 ml. It is, however, now felt that waters, prior to chlorination, may have bacterial counts which exceed 50 <u>Esch</u>. <u>coli</u> per 100 ml. Butterfield (1943) used a density of 2000 bacteria per ml on the assumption that "it was not in excess of the number which might be expected in many waters." Discussing the relative concentration of <u>Eber</u>. <u>typhosa</u> and <u>Esch</u>. <u>coli</u> in sewered area in which the annual typhoid rate is as high as 2000 per 100,000 population, Kehr and Butterfield (1943) expected a ratio of 100 to 1,000,000. Due to its relative abundance and to its high resistance to disinfection, <u>Esch</u>. <u>coli</u> has been widely selected as a test organism. (There are other reasons also.) This is, however, a serious question as to whether the destruction of <u>Esch</u>. <u>coli</u> also reflects the destruction of water-borne virus.

Recently, Geldreich et al., as quoted by Clarke et al. (1962), showed that the average coliform density feces per capita per day is 1.95×10^9. Using this data as well as Sabin's (1955) on virus,

Clarke (1962) found that the relative enteric virus density to coliform density in human feces is about 15 virus units for every million coliforms (a 1 to 65000 ratio). In another extensive survey conducted at the Robert A. Taft Center and quoted by Clarke (1962), a calculated density of 700 virus units per 100 ml of sewage and 0.15 to 1.5 virus units per 100 ml of polluted surface water was determined. Comparing his theoretical data with that of Kelly (1952), Clarke (1962) concludes that "the average enteric virus density in domestic raw sewage is probably 500 virus units per 100 ml, and in polluted surface water is not more than 1 virus unit per 100 ml."

2.5 Interim Solution

If the available data is accurate, it appears then that *Esch. coli* should continue to be the test organism so long as all enteric viruses are almost equal in resistance to various methods of disinfection. However, Chang (1968) questions the validity of the data on virus on the basis of the following arguments:

1. There are a large number of sporadic cases of viral infections, especially of virus (or viruses) of infectious hepatitis and poliomyelitis, throughout the world showing thereby that a low level of transmission of virus is occurring in spite of water and wastewater treatment in those areas. The situation is worse in less sanitated regions, due apparently to more severe pollution of the raw water and a lower water treatment efficiency.

2. So far we do not have a method suitable for the detection of enteroviruses in water, especially in small numbers.
3. The question of whether infectious hepatitis is caused by one virus or a number of viruses is still unresolved. In addition, the relative resistance of the viruses has not been established.

Pending the availability of such a method of viral detection and enumeration plus more information regarding the virus of infectious hepatitis, no reliable comparison can be made between a test organism such as _Esch_. _coli_ and some representative virus. The following suggestions should be considered until then:

1. If polluted water is used as a source and if cases of enteric viral diseases occur without a known mode of transmission, the water treatment processes should be examined (Chang 1968).
2. Efforts should be undertaken to revise existing standards for _Esch_. _coli_ established by U. S. Public Health Service. This should be done on the basis of existing data with an added safety factor (Personal communication - 1).
3. Wherever and whenever possible, especially in large cities where laboratory facilities are available, virus detection in the raw and finished water of municipal supplies with the present methods of detection should be a regular practice. As far as possible, disinfection dosages should be determined on this basis if it exceeds the dosage presently required for the destruction of _Esch_. _coli_. (Personal communication -1).

Chapter 3

OUR CHIEF SENTINELS

3.1 Introduction

Until recently, it would not have been an exaggeration to say that "disinfection" has been almost synonymous with "chlorination." The importance of chlorine as a disinfecting agent can be estimated from the figures reported by the United States Public Health Service (Thomas, 1953) which show that in 1948, 43.9% of all existing water treatment facilities employed chlorination as the only treatment. Cook (1965) reports further that in the same year 6135 plants representing some 88% of the existing facilities and serving more than eighty million people, employed chlorine disinfection alone or in conjunction with other treatment processes. This represents, according to him, more than 86% of the population served by all community water supplies, both with and without treatment, and some 96% of the population receiving treated water.

Although the situation has not changed much since that time, considerable interest in other disinfecting agents has developed. Other methods of disinfection which show great potential for the future include the following disinfectants:

1. Iodine
2. Ozone
3. Bromine
4. Ultraviolet rays

In addition, the following methods of disinfections need be

explored further before they could be accepted as possible disinfectants in the future:

5. Chlorine Dioxide
6. Silver
7. Copper

3.2 Disinfection by Halogens

There are two major reactions which take place during disinfection by the halogens. The first of these is a hydroloysis reaction:

$$X_2 + H_2O \rightleftharpoons HOX + H^+ + X^- \tag{1}$$

The second is the ionization of the hypohalous acid formed during hydrolysis:

$$HOX \rightleftharpoons OX^- + H^+ \tag{2}$$

where X represents chlorine, iodine or bromine.

These reactions are rapid and an equilibrium is formed almost at once in which varying quantities of the possible active species X_2, XOH and OX^- are present (Harvard Report, 1945).

A knowledge of the equilibrium constants for the reactions would give:

$$\frac{[HOX] \quad (H^+) \quad [X^-]}{[X_2]} = K_h \tag{3}$$

and

$$\frac{(H^+) \quad [OX^-]}{[HOX]} = K_i \tag{4}$$

where

K_h = hydrolysis constant

K_i = ionization constant

The total analytical concentration, C, of the oxidizing halogen, in moles per liter, can be expressed by the relation:

$$C = HOX + OX^- + X_2 \tag{5}$$

The analytical methods employed for the halogens determine the sum of the quantities of these three constituents and do not distinguish one specie from the other (Fair et al., 1947).

Solving the above five equations, we get

$$[X_2] = \frac{(H^+)\ [X^-]\ C}{K_h}\left(\frac{1}{1 + K_i/(H^+) + \frac{(H^+)\ [X^-]}{K_h}}\right) \tag{6}$$

$$[HOX] = C\left(\frac{1}{1 + K_i/(H^+) + \frac{(H^+)\ [X^-]}{K_h}}\right) \tag{7}$$

$$[\bar{X}] = \frac{CK_i}{(H^+)}\left(\frac{1}{1 + K_i/(H^+) + \frac{(H^+)\ [X^-]}{K_h}}\right) \tag{8}$$

Thus the concentrations of the three halogen components can be computed knowing the hydrolysis constant, the ionization constant, the pH of the solution, the total concentration of active halogen and the halide ion concentration.

3.3.1 Chemistry of Chlorination

The hydrolysis and ionization constants for chlorine are:

$K_h = 3.8 \times 10^{-4}$ at 20°C

(Harvard Report 1945)

$K_i = 3.3 \times 10^{-8}$ at 20°C

Calculations using the equilibrium equations indicate that for all concentrations of chlorine used in water disinfection, the percentage of chlorine as Cl_2 is so small that it can be disregarded.

In fact it is somewhat of a misnomer to call the process "chlorine-disinfection," since Cl_2 is present for less than a second in water. Based on above values of K_h and K_i, Harvard Report (1945) reported the following relative amounts of hypochlorous acid and hypochlorite ion at various values of pH:

TABLE 3.1

PERCENTAGES OF CHLORINE SPECIES PRESENT IN DILUTE CHLORINE SOLUTIONS AT VARIOUS pH LEVELS

TITRABLE CHLORINE CONCENTRATIONS = 1 mg/l

pH	%HOCl	$\%OCl^-$
4 and below	100	0
5	99.7	0.3
6	96.8	3.2
7	75.2	24.8
8	23.3	76.7
9	2.9	97.1
10	0.30	99.7
11	0.03	99.97

Similar results were obtained by Wattie and Butterfield (1944).

Thus, for a particular temperature, the relative quantities of hypochlorous acid and hypochlorite ion are a function of the hydrogen ion activity or pH. Since analytical methods so far available determine the sum of the two species, a knowledge of pH is required to determine the quantities of the individual species. It was probably an effort to be consistent with the analytical determination that the AWWA committee which prepared the chapter on "Chlorination and other disinfecting practices" for the manual on "Water Quality and Treatment" in the late forties introduced the terms, "free available chlorine" and "combined available chlorine."* Unfortunately, these terms are somewhat confusing and misleading. Although HOCl is far more powerful a disinfectant than hypochlorite, the two are lumped together as part of the "free available chlorine" (Chang 1968). Berg (1964) complains of this as "poor semantics."

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* The AWWA Manual (1951) defines the terms as follows: "That chlorine existing in water as hypochlorous acid and hypochlorite ions is defined as free available chlorine."

"That chlorine existing in water in chemical combination with ammonia or organic nitrogen compounds is defined as combined available chlorine."

3.3.2 Chlorine Demand and Chloramines

The concentration of the chlorine available for disinfection is greatly affected by the presence of oxidizable organic matter as well as nitrogenous substances. "Chlorine demand" may be defined as the quantity of chlorine involved in side reactions with substances in water that consume or destroy chlorine residual. Formation of chloramines is the result of side reactions of the disinfectant with substances present in water that transform the active ingredient (HOCl) into NH_2Cl, $NHCl_2$ or NCl_3. These chloramines are far less potent germicides than HOCl. Although this latter phenomenon has a marked influence on the process of chlorination for disinfection, it is not generally well understood. Morris (1967) points out that "as this survey of available data has shown, current knowledge of the rates and mechanisms of reaction of dilute aqueous chlorine with nitrogenous compounds is very incomplete and scattered." The following is a summary of the data which the literature reveals: (Sawyer (1967), White (1968), Fair (1968) Butterfield (1946)).

1. The three basic equations that govern the formation of chloramines are:

$$NH_3 + HOCl \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O \qquad (9)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 \text{ (dichloramine)} + H_2O \qquad (10)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 \text{ (trichloramine)} + H_2O \qquad (11)$$

According to these equations 3 moles of chlorine are required to react with each mole of ammonia. In practice only 2 moles are required.

The addition of chlorine in water treatment practice beyond this amount required to react with ammonia is called "break point chlorination." Chlorination beyond the break point results in the formation of a "free chlorine residual."

2. The rate of the equation (9) is highly dependent upon the pH of the solution. The maximum rate occurs at a pH of 8.3 and decreases rapidly at higher and lower pH values.

3. With molar ratios of chlorine to ammonia up to 1:1, both mono- and dichloramine are formed. The relative amounts of each are a function of pH, and greater proportions of dichloramine appear at lower pH values according to the following expression:

$$2\ NH_2Cl + H^+ \rightleftarrows NH_4^+ + NHCl_2 \qquad (12)$$

Further increases in molar ratios result in the formation of the gases NCl_3 and N_2.

4. Chloramine residuals usually reach a maximum when 1 mole of chlorine has been added for each mole of ammonia. They then decline to a minimum value at a chlorine-to-ammonia ratio of 2:1.

5. The germicidal powers of the chloramines are different for different organisms. These shall be discussed later.

Thus, the formation of chloramines are dependent upon a number of factors such as pH, chlorine-to-ammonia ratio, temperature, contact time and salinity.

3.3.3 Germicidal Properties of Chlorine and Its Various Species

While the disinfection of water by chemical agents is a function of a number of variables, the following discussion is restricted to the resistance of a single organism to its destruction by one species of the disinfectant. Several other variables are assumed constant at that time:

1. The temperature of the water
2. The composition of the water
3. The concentration of the organisms
4. Presence of other organisms

Morris has done a survey of the literature for the comparative germicidal efficiencies of various disinfectants. (Personal communication -2). His analysis is presented in Table 3.2.

TABLE 3.2

CONCENTRATIONS (mg/l) OF FORMS OF ACTIVE CHLORINE TO YIELD 99 PERCENT GERMICIDAL EFFECT IN 10 MINUTES AT 25°C

Organism	$HOCl$	OCl^-	NH_2Cl
Esch. coli	0.005	0.6	1.0
poliovirus type 3	0.02	>> 1	25.0
cysts	2.00	800	10
schistosomes	0.5-1.0	-	0.4

This data points out that hypochlorous acid is the principal disinfecting agent irrespective of the type of organism. Hypochlorite ion and monochloramines are far less potent in their germicidal

action. This is actually true for all temperatures and contact times. Dichloramine is slightly more powerful than monochloramine but neither compares with hypochlorous acid. These facts are amply supported by other sources in the literature (Butterfield (1948), Chang (1968), Kabler (1951), Berg (1964), Kabler (1961)).

3.4.1 Chemistry of Iodination

The equilibrium constants for the hydrolysis and ionization of iodine are:

$$K_h = 3 \times 10^{-13} \text{ at } 25^{\circ}C$$

$$K_i = 4.5 \times 10^{-13} \text{ at } 25^{\circ}C$$

Using these values in equations 6, 7 and 8, Chang (1958) calculated the effect of pH on the reactions for total titrable concentrations of iodine from 0.5 to 50.0 ppm. Three conclusions may be drawn from his calculations which were presented in graphical form:

1. As pH increases from 5.0 to 8.0, molecular iodine (I_2) hydrolyzes to form hypoiodous acid (HOI).
2. As the titrable iodine concentration increases, hydrolysis takes place to a lesser degree.
3. Very little ionization of hypoiodous acid takes place at the pH values encountered in ordinary water disinfection practice.

To illustrate these points, Table 3.3 has been prepared on the basis of curves presented by Chang.

TABLE 3.3

EFFECT OF pH ON THE HYDROLYSIS AND IONIZATION OF IODINE

	Titrable Iodine = 1 mg/l			Titrable Iodine = 5 mg/l		
	% Concentration of			% Concentration of		
pH	I_2	HOI	IO^-	I_2	HOI	IO^-
5	99	1	0	100	0	0
6	95	5	0	98	2	0
7	67	33	0	90	10	0
8	20	80	$\ll 1$	55	45	0

In addition to hydrolysis and ionization two other phenomena are important in iodine disinfection. They are of great significance because the products formed have practically no germicidal activity (Black (1965), Chang (1966)). The first phenomenon is the formation of iodate and iodide at or above a pH of 8 due to the instability of hypoidous acid. The reaction can be shown to take place as follows:

$$3\ HOI + 2\ (OH^-) \rightleftarrows HIO_3 + 2H_2O + 2I^- \qquad (13)$$

Wyss and Strandskov (1945) showed, however, that this reaction is strongly influenced by the buffer used and the concentration of titrable iodine. In case of carbonate buffer, which normally predominates in natural waters, this reaction is quite slow. Moreover, below a concentration of 30 mg/l of titrable iodine, the formation of iodate is not substantial. Black (1965) carried out studies on iodate formation at titrable iodine concentration in the range of 0.5 to 3.0 mg/l and reported that no significant amounts of iodate

were formed in the concentrations and within a pH range of 5.0 to 9.0.

The second important phenomenon which influences iodination is the formation of tri-iodides or polyiodides. This reaction takes place in all iodine preparations used for disinfection which contains enough iodide to give an $I_2:I^-$ molar ratio of 1:1 or less. The reaction taking place is

$$I_2 + I^- \rightleftarrows I_3^- \qquad (14)$$

$$I_2 + I_3^- \rightleftarrows I_5^- \qquad \text{and so on} \qquad (15)$$

$$\frac{[I_2]\ [I^-]}{[I_3^-]} = K_{i_3} \qquad (16)$$

The value of K_{i_3} at $25^oC = 1.4 \times 10^{-3}$. Chang (1958) investigated this reaction and has reported that the formation of the triiodide ion or higher iodides is insignificant at the iodide concentrations likely to be found in water disinfection. This was earlier reported in the Harvard Report (1945).

3.4.2 Chemical Demand and Formation of Iodamines

The Harvard Report (1945) states that:

1. Iodine demands of natural waters are of approximately the same magnitude as chlorine demands on a weight (mg/l) basis. On a molar basis, iodine demands are approximately 28% of the chlorine demand.
2. There is no evidence for the reaction of iodine with ammonia or amino type substances in aqueous solutions.

Similar findings were reported by Black (1965).

3.4.3 Germicidal Properties of Iodine and Its Various Species

As discussed in Section 3.4.1, of the five species of iodine which might exist in water upon its application in its commercial form, only molecular iodine and hypoiodous acid are important. These species alone are the powerful disinfecting agents.

Comparing the disinfection efficiencies of the two species, Carrel et al. (1957) reported that HOI is three to four times as active as I_2 in killing Esch. coli. In the killing of spores (B. metiens), Wyss and Strandskov (1945) claimed that I_2 is at least three times more effective than HOI. Clarke, et al. (1964) showed that the viricidal efficiency of hypoiodous acid is 40 to 50 times as great as molecular iodine when tested against the hardy group of enteric virus.

Chang (1967) compiled data for the time-concentration relationship for 99.9% destruction of the accepted test organisms from bacteria, protozoa and virus at 18°C. The titrable iodine concentrations in mg/l of I_2 and HOI for a contact time of 10 minutes are given below.

TABLE 3.4

CONCENTRATIONS OF IODINE SPECIES FOR 99.9% KILL
FOR 10 MINUTES CONTACT TIME AT 18°C

Organism	Molecular Iodine - mg/l	Hypoiodous Acid - mg/l
Esch. coli	< 0.005	$\ll 0.005$
Poliovirus Type 1	$>$ 20	0.5
E. histolytica	2.5	4.0

From this data it appears that molecular iodine is about twice as powerful as hypoidous acid for cysts of E. histolytica, whereas hypoiodous acid is superior to I_2 in the disinfection of bacteria and virus.

3.5 Disinfection with Bromine

A survey of the literature reveals very little data on the use of bromine in the disinfection of water in general and on the chemistry of bromine in particular. The Harvard Report (1945) used the following values of the hydrolysis constant and ionization constants for calculating concentrations of bromine species in dilute aqueous solutions of bromine:

$$K_h = 5.8 \times 10^{-9} \text{ at } 25^{\circ}C$$

$$K_i = 3.75 \times 10^{-9} \text{ at } 25^{\circ}C$$

The Harvard Report also indicates that the value of the ionization constant needs more study. Jolly (1966) reports the value of K_i as 2.1×10^{-9} at room temperature.

In any case, the values of the above constants are such that "within the range of pH values encountered found in water supply

work any one of the three possible species, i.e., Br_2, HOBr and OBr^-, may predominate." (Harvard Report,1945). The following are the concentrations of various bromine species in a solution containing 1 mg/l of titrable bromine as recorded in the Harvard Report.

TABLE 3.5

PERCENTAGES OF BROMINE SPECIES PRESENT IN DILUTE BROMINE SOLUTIONS AT VARIOUS pH LEVELS FOR TITRABLE BROMINE CONCENTRATION OF 1 mg/l

	pH								
Species	3	4	5	6	7	8	9	10	11
Br_2	45.3	11.8	1.5	0.2	-	-	-	-	-
HOBr	54.7	88.2	98.5	99.6	98.0	83.3	33.3	4.8	0.5
OBr^-	-	-	-	0.2	2.0	16.7	66.7	95.2	99.5

At higher pH values and at long contact times, there is further decomposition of hypobromite into bromate and bromide according to the equation:

$$3\ OBr^- \rightarrow BrO_3^- + 2\ Br^-$$

As shall be discussed later, OBr^-, BrO_3^- and Br^- have very poor germicidal power and as such their formation is a positive drawback in bromine disinfection. It is, however, yet to be determined whether these reactions play an important role in dilute aqueous solutions.

"There is no evidence for the formation of compounds between bromine and ammonia in water solution" (Harvard Report, 1945). It was then believed that these substances were completely hydrolyzed at the concentrations employed in water disinfection practice.

Galal-Gorchev and Morris (1965), however, hold the view that there is rapid reaction between bromine or hypobromite and ammonia in dilute buffered aqueous solutions which results in the formation of NH_2Br, $NHBr_2$ or NBr_3, depending upon pH and molar ratio of ammonia to bromine. According to these investigators, NH_2Br predominates in alkaline solutions at high N/Br ratios, $NHBr_2$ predominates in the pH range 6-9 with N/Br ratios about 5 to 20, and NBr_3 predominates in more acid solutions. NBr_3 is found in mixtures up to pH 8 when two to three moles of bromine per mole of ammonia are allowed to react. Similar findings were reported earlier by a number of researchers, primarily Johannesson (1960).

Since the formation of bromamines has been confirmed only recently, it appears that no work has been carried out with respect to their germicidal activity. The literature contains relatively few references to studies of the disinfecting efficiencies of Br_2 and HOBr. In fact, Chang (1968) writes that "very little is known of the viricidal efficiency of HOBr." Whatever data is available is not even accompanied by data on pH. Therefore, the concentrations of the bromine species present cannot be calculated. In general, bromine has been reported to be less viricidal than chlorine or iodine on a weight basis. Morris (Personal communication -2) found that the concentration of HOBr required to obtain a 99% kill in a contact time of 10 minutes at 20-25°C are 0.05 mg/l and 10 mg/l for <u>Esch. coli</u> and <u>Endamoeba histolytica</u> respectively. Marks and Strandskov (1950) reported the results of tests with <u>B. metiens</u> where molecular bromine was found more active than hypobromous acid.

On the whole the germicidal behavior of bromine and its derivations are not very well known.

3.6 Ozonation

Ozone disinfection is another method which has potential of an effective and economical technique. It has not been extensively used in the U.S. The chemical and physical properties of ozone are not yet adequately known. This is probably one reason which has obstructed the collection of consistent data on the germicidal properties of ozone.

Ozone is a very powerful oxidizing agent and reacts more rapidly with organic substances than hypochlorous acid. This may indicate that the disinfecting rate might be faster with ozone. However, at the same time, the "ozone demand" of natural waters would be expected to be larger than the corresponding chlorine demand.

Another serious drawback of ozonation is its instability in solution. It decomposes into oxygen. Stumm (1958) quoted his earlier work (Stumm (1954) when he showed that this decomposition in aqueous solution is temperature dependent, is strongly catalyzed by trace concentrations of many organic and inorganic constituents of water and is especially dependent on the hydroxyl ion concentration. For all these reasons there is no residual concentration of ozone in water distribution lines after ozonation.

Regarding the germicidal efficiencies of ozone there are widely diverging reports in this literature. Stumm (1958) analyzes the data available and reports that, on the whole, ozone is a better

bactericidal, viricidal and cysticidal agent than hypochlorous acid when judged on the basis of contact time alone.

Morris (Personal communication - 2) finds the following representative figures in the analysis of the literature on ozonation:

TABLE 3.6

CONCENTRATIONS OF OZONE FOR 99% KILL IN 10 MINUTES AT 20-25°C

Organism	O_3 Concentration in mg/l
Esch. coli	0.001 (at 5°C)
Endamoeba histolytica	0.1
Poliovirus	0.03 (type not known)

Chang (1968) quotes Trahtman's unpublished data (1966) which showed that 99.9% destruction of enteroviruses was achieved with 0.2 ppm of ozone. The temperature and contact time here not given.

Faber (1961) quotes French sources which state that the Water Control Service of the city of Paris used 0.1 mg/l of ozone for a contact time of 5 seconds against 60,000 E. coli/ml.

On the whole, it appears that ozone has disinfecting powers against the water-borne pathogens in water comparable to that of chlorine. However, much work is required to authenticate the available information.

3.7 Other Processes

All processes other than those already discussed, with the exception of the application of heat, are in their infancy. The boiling of water for disinfection purposes is an ancient process and

is a "safe and commendable practice where drinking water safety is a suspect," write Fair et al. (1968). All other methods may be said to be in an experimental stage.

Chapter 4

QUEST FOR THE BEST

4.1 For over fifty years in the U.S. chlorine has been the dominant choice as a disinfectant for drinking water. It has performed so great a service to man that it has become a standard. It has gained such wide acceptance that any effort to substitute another agent in its place, even for experimental purposes, is reviewed with skepticism by those in waterworks practice. At the same time some researchers feel that other possible disinfectants may have more potential.

4.2 Criteria for Selection

What criteria should determine the choice of disinfectant for the disinfection of different waters? There are numerous variables which are involved. In this chapter consideration will be given to a few of the prominent factors which influence disinfection.

A. Physical and Chemical Characteristics of the Water to be Treated:

(a) Chemical demand: In the practice of chlorination, the term "chlorine demand" refers to the amount of chlorine which must be added before a stable residual is formed. Since this forms an important fraction of the dose of a disinfectant, its determination is very important.

If the demand for disinfectant is high, higher dosages of disinfectant may be uneconomical or have undesirable tastes and odors. Under such conditions, iodine, for which the chemical demand is low, or pre-ozonation might be considered. Chang (1968) refers to ozone

as "ideally suited for treating water prior to chlorination to reduce the chlorine demand as well as the pathogen load, thus making the chlorination process more satisfactory and less objectionable on the basis of odor and taste." Since ozonation must be performed on-the-spot, it may not always be applicable. For these reasons, iodine has been selected by the military for disinfection of water under field conditions.

(b) Ammonium ion concentration: A knowledge of the ammonia-nitrogen concentration of the water to be disinfected is required. This information will permit the calculation of formation of chloramines which may be less germicidal or have no disinfecting power at all. On the other hand, iodine does not undergo reactions with nitrogenous matter (Harvard Report, 1945; Black, 1965).

(c) pH: We have discussed in earlier chapters the influence of pH on the hydrolysis, ionization and decomposition of a halogen in water. It has also been observed that these reactions transform the original substance into those which may or may not have any resemblance to the parent element. In the case of chlorine, for example, the increasing ionization of hypochlorous acid into hypochlorite ion with rising pH values reduces the disinfecting ability of the aqueous solution of chlorine. Fig. 4.1 has been prepared to present the influence of pH on chlorine, bromine and iodine solutions. They are based on data presented in Chapter 3 for 1 mg/l of titrable halogen. These curves show that pH 7.5 can be regarded as a critical pH for chlorination because at higher pH the hypochlorite

Principal Disinfecting Agents in Halogens are:

1. Hypochlorous Acid
2. Molecular Bromine/Hypobromous Acid
3. Molecular Iodine/Hypoiodous Acid

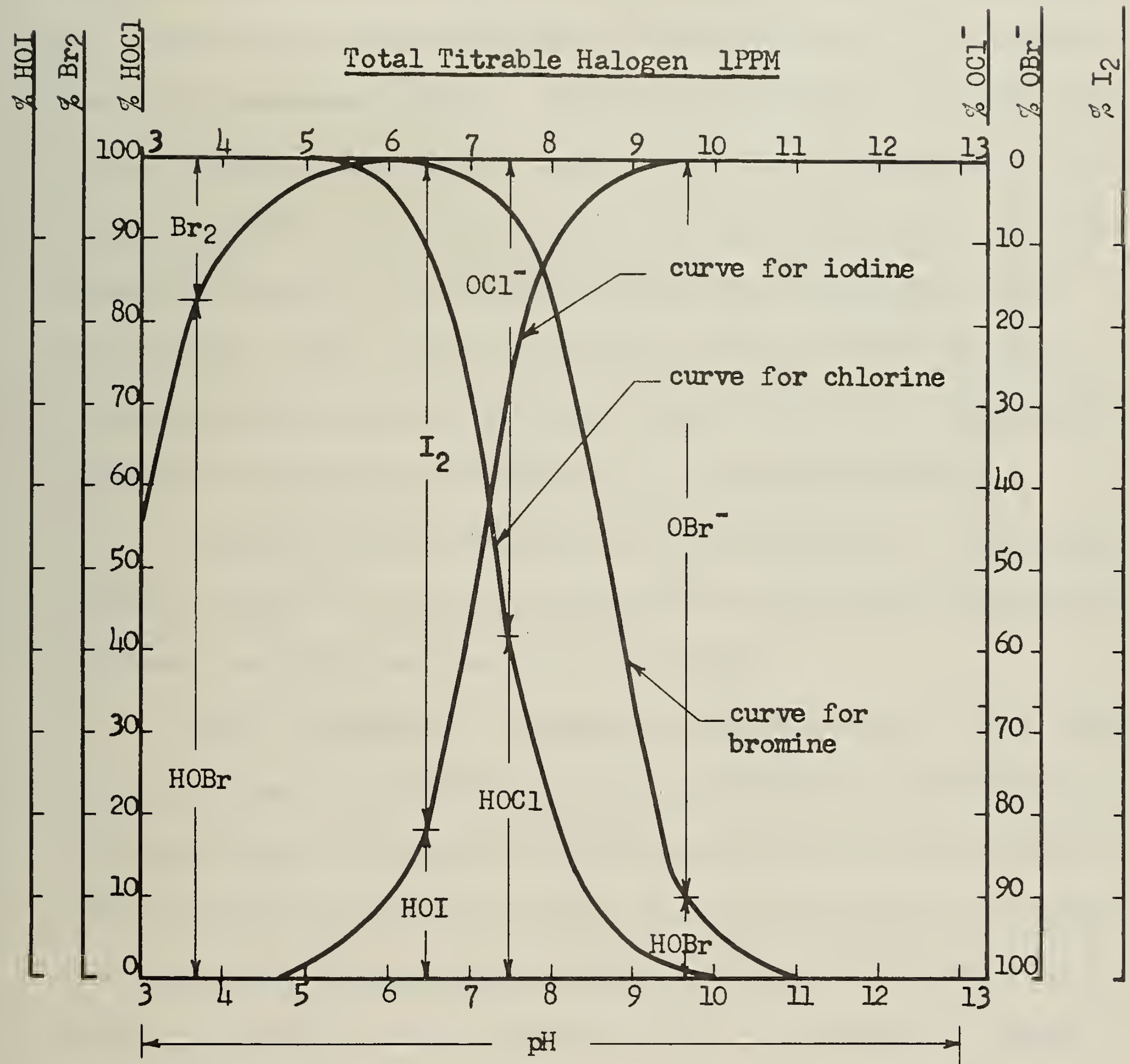

FIGURE 4.1. PERCENTAGES OF VARIOUS SPECIES AT DIFFERENT pH VALUES

concentration increases sharply. These high pH values are encountered where softening is practiced.

The iodine curve in the same figure reveals increasing hydrolysis of molecular iodine into hypoiodous acid with increasing pH. Hypoiodous acid predominates in the region, pH 7.3-9.0, after which it decomposes rapidly. Comparing the behavior of iodine with that of chlorine over this pH range, iodine has an advantage in that both hypoiodous acid and iodine are good disinfectants and, in fact, hypoiodous acid is a far better viricidal and bactericidal agent than iodine. Thus, iodine is effective over the entire pH range whereas chlorine becomes ineffective above pH 7.5. The disinfecting powers of the species, HOBr and Br_2 are not yet established.

Thus, pH plays a major role in the selection of the disinfectant in spite of the fact that the final choice would involve the ultimate economy, human reaction and safety.

(d) Temperature: Temperature should not play a very critical role in water disinfection basically because the temperature of the water usually available for disinfection does not vary widely. In addition the temperature effects on the rate of kill are parallel for almost all disinfectants and conform closely to the Van't-Hoff-Arrhenius equation (Harvard Report 1945*). In the case of disinfecting tablets, the water temperature does have an effect on the rate of solution.

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* Berg (1964) reports that within the biological range, a 10°C decrease in temperature would increase the contact time for a given amount of viral destruction by 350 to 450% in case of molecular I_2 and by 200 to 300% in case of chlorine.

B. Governing Organism:

If a single organism is to be used, which organism should be regarded as the governing organism (one who would dictate the dosage or residual requirements of the disinfectant)? Considering the threat of the virus, Chang (1968) comments that "we must base ourselves on circumstantial evidence, and not on epidemiologic dogma, in ascertaining the role of water supply in viral transmission in nonepidemic times." The coliform index as the minimum standard should not be relied upon. Instead, the water should be made safe from viral infections without sacrificing other desirable properties. This can be illustrated by the example of a municipality reporting low level viral infection and whose treated waters have pH reactions around 8.5. Such a water can be disinfected satisfactorily with high dosages of chlorine. But, as an alternative, iodine can be used.

In areas where waterborne amebic dysentery is reported to have a high incidence, it is improper to rely on chlorination unless it is accompanied by effective filtration and other treatment. This is because hypochlorous acid is a very poor cysticidal agent. On the other hand, molecular iodine, and not hypoiodous acid, is effective against Endamaeba histolytica.

C. Odors and Tastes:

Apparently it may not seem to be a critical element in our criteria at present. Tastes and odors might pose a serious problem in the near future. With increased stream pollution, larger doses of disinfectants and their residuals might become inevitable. Morris

(1966) insists that "a minimum residual concentration of 1 to 2 ppm of free chlorine after 10 to 30 minutes of contact must become standard practice with all waters that have been subjected to any sizable degree of contamination." With an increased concentration of chlorine for disinfection coupled with the presence of phenolic substances (even though USPHS has set an upper limit of 1 ppb on phenolic compounds!) plus the formation of chloramines, the problems of tastes and odors will increase. Such problems may be less severe with iodine but it does not appear to be absent. Black (1965) concludes that "when the concentration of elemental iodine is 1.5-2.0 ppm, many people will be able to detect a taste, but it will not be an objectionable one." This statement concedes that taste, whether sweet or otherwise, would be present in solutions containing molecular iodine. Where iodine is to be used as a viricidal agent, it should be present in the form of hypoiodous acid which is highly viricidal. Since HOI has been reported to be a colorless and tasteless substance (Browne (1968)), this problem should be minimum at high pH.

While ozone is not accepted as a full fledged disinfecting agent, it has great potential as a prechlorination agent both for the elimination of chlorine demand as well as for the removal of color, odor and taste problems. Stumm (1958) stresses the great capability of ozone and Chang (1968) recommends the use of ozone prior to chlorine disinfection.

Morris (1966), however, prefers superchlorination followed by dechlorination using agents such as SO_2 or activated carbon.

D. Concentration - Contact Time Relationships

Flexibility in the selection of the concentration of the disinfectant for a corresponding contact time, during which the required percentage kill is obtainable, is desirable.

Fair and Geyer (1968) reproduces from literature the following empirical formula:

$$C^n t_p = K$$

where

C = concentration of the disinfectant

t_p = time required to effect a constant percentage kill of the organism

n = coefficient of dilution or a measure of the order of the reaction

K = a constant

n & K depend upon the organism being disinfected, temperature and the disinfectant

Values of n & K for some conditions have been reported (Berg 1964; Kimball 1953; Gurian 1956).

E. Cost of Disinfection

The cost of gaseous chlorine and iodine in 1961 was reported to be \$0.0625 per pound and \$1.10 per pound respectively (Chamber, 1961). This would place the cost of iodination roughly 18 times higher than that of chlorination on purely purchase price basis. Beattie (1968) reported almost the same prices and cost proportion.

Diaper (1968) reported on the cost of ozonation for water sterilization on the basis of 1 ppm of ozone. His analysis showed

that installation cost (which includes ozone generator and air preparation equipment and electrical equipment, but no construction work) is almost constant beyond a rated capacity of 10 mgd water treatment plants and is about $5000 per mgd treated. The capital cost up to 2 mgd plants is around $15,000 per mgd treated but then falls rapidly. The operating costs for ozonation chiefly depend upon the cost of electricity and was reported by him to be 0.1¢ per 1000 gallons at a dose of 1 ppm. This cost includes electrical consumption for ozone production and injection, air preparation and ancilliaries. The average cost for installation and operation based on a dosage of 1 ppm ozone over a period of 20 years at 4% interest plus taxes for a 10 mgd plant comes to 0.28¢ per 1000 gallons.

On a personal communication with local water treatment plants with a peak capacity of 22 mgd (Smith, 1968), it was gathered that the cost of chlorination was about 0.2¢ per 1000 gallons. Making a rough comparison with ozonation costs, it appears that ozonation is only about 50% more costly than chlorination. This means that even if ozonation is not indepently relied upon, preozonation followed by chlorination may be a feasible yet not a very uneconomical proposition. This should, of course, ensure a more satisfactory disinfection than chlorination alone.

On a rough estimation of the cost of iodination on the basis of purchase price of iodine and chlorine, it might cost around 4¢/ 1000 gallons. Black (1965) has tried to offset this high cost of iodination on the following basis:

1. Iodine being a weak element chemically has substantially lower iodine demand both for organic matter content of most waters as well as for nitrogenous substances.

2. Iodide ion may be reconverted to the elemental form "by a wide variety of oxidizing agents, weak and strong." Presence or introduction of such an oxidizing agent should be able to increase the residual contact time with water manifold. He calls this idea "unique in water disinfection practice." Indeed it is so but the question refers back to how much price does one attach to this insurance for public health. Another problem posed by this idea will be the discovery of an ideal oxidant which can be introduced in drinking water safety and without enhancing the overall cost substantially.

3. Little decomposition of hypoiodous acid in the pH range and concentrations likely to be encountered in water disinfection practice is the third factor offered by him. Probably the comparison is with the ionization of hypochlorous acid in chlorine solutions in the same pH range. While the comparison is well taken, it appears that this factor counts towards the determination of dosage of iodine in our criteria rather than as a separate evaluation.

In addition to the above factors, one may agree to additional reduction due to greater acceptability of iodine by the user on the basis of lesser degree of odor, taste and color problems as well as elimination of safety hazards usually associated with the use of liquid chlorine. There are numerous accidents on record which have prompted plants to stop the use of liquid chlorine and to switch

over to hypochlorites. One such organization was a sewage treatment plant in New York City which made this decision in 1963 (Cook, 1965). Of course, this decision cannot be easily made for a water treatment plant because of the seriousness of the purpose of disinfection in water supply systems. The use of hypochlorite should raise the pH, thus converting hypochlorous acid into hypochlorite ion which has, comparatively, little germicidal power.

Thus, the economic comparisons are not as easy as they appear to be but need deeper investigations and realistic evaluations.

4.3 Variables involved in "quest for the best" are many and complex. There may be a few more that can be added to the above list. However, the idea suggested here is that a flexible and critical approach based on the evaluation of the needs and availability should be attempted rather than pursuing a rigid and biased line of thought.

Chapter V

THE PILL

5.1 There are many occasions when water disinfection must be practiced on a small scale and under adverse conditions. The need for a ready-to-use disinfectant is greatest during military operations or at times of natural disasters when small groups of people or even individuals have to depend upon sources of water which might be contaminated. Even during peace time, campers, sportsmen and adventurers have need for a packaged, instant-disinfectant such as a tablet. This need was first recognized more than fifty years ago (Morris et al., 1953). However, only a few preparations, usually consisting of iodine and chlorine, were in use at the beginning of the Second World War. At that time a team of scientists and engineers conducted an extensive investigation at Harvard University under a contract with the Committee on Medical Research of the Office of Scientific Research and Development. The Harvard researchers (Harvard Report, 1945) listed the following desirable properties of chemical disinfecting agents which are intended for use under field conditions:

A. This should be made available as a tablet of such size as to permit use of a single or at most two tablets for a small quantity of water.

B. The technique of applying the disinfectant should be simple of management, substantially foolproof, and not unduly time consuming.

C. The agent should disintegrate or dissolve quickly and liberate its active ingredient or ingredients rapidly in order to free as much time as possible for the kill.

D. Dosages should preferably be such as to ensure disinfection of all kinds of natural waters to be treated without testing for residual concentrations of the disinfectant.

E. The treated water should be acceptable to the user. In other words, odor, taste and appearance of the water should not be objectionable and foods and beverage powders or concentrates placed in the water should not be changed in normal appearance or flavor.

F. The treated water should not be toxic or otherwise undesirably physiologically active during periods of reasonable use. The water, furthermore, must not interfere with essential prophylactic or therapeutic medication.

G. The treated water should not be corrosive to water containers.

H. The disinfecting agent should be stable under conditions of storage and actual use.

I. The ingredients required in compounding the disinfectant should be economically and strategically available.

J. Manufacture of the chemical agent should lend itself to large scale preparation with normally available chemical and pharmaceutical equipment.

5.2 Ingredients of a Tablet

Apart from disinfectant, a tablet must have substances which help either in the manufacture or its dissolution or promotion of disinfecting process. These ingredients could be classified as follows:

A. Filler

A filler or an excipient is always required in pharmaceutical practice to give the tablet adequate bulk. A number of fillers are available but a disinfecting tablet must employ one which is soluble (to preserve the clarity of the treated water), and at the same time should not be hygroscopic and should be inert to the disinfecting chemical. As shall be discussed later, the halazone tablet has sodium chloride as an excipient. A number of soluble nitrates, phosphates, acetates and sulfates could also be usefully employed.

B. Buffer

The selection of a buffer to promote the disinfecting action of the agent is very important. For example, for any chlorine compound to be an effective disinfectant, it is essential that the pH of the chlorinated water be less than 8. Above pH 8, the predominance of hypochlorite ion seriously reduces the disinfection capability. Similarly, where iodine is used, the pH of the solution should not be less than 7. Otherwise, the viricidal efficiency of hypo-iodous acid will be sacrificed. Sometimes, the buffer also

serves as a filler. This is true of globaline tablets which employ disodium dihydrogen pyrophosphate as a buffer as well as an excipient.

C. Lubricant

The function of this ingredient is to lubricate the punches of tablet-making machines. Talc is a popular lubricant. Calcium or magnesium stearate are also sometimes added. The purpose of a lubricant may sometimes be performed by the filler itself.

D. Swelling Agent

The use of certain colloidal clays, such as bentonite, promotes the disintegration of tablets by quick swelling in water causing the tablet to burst. This clay is chemically inert but physically very active.

5.3 Test Organism

Emergency conditions demand that the disinfecting agent or tablet should be capable of killing the most resistant water-borne pathogen. The Harvard Report (1945) states in this regard that "leaving out of consideration the virus of infectious hepatitis, the cysts of Entamoeba histolytica appear to be the most resistant water-borne pathogens that must be dealt with in the water disinfection and so appear to determine the pattern of accomplishment that must be established both in the laboratory and in the field." Much work has since been carried out on various human enteroviruses and the results confirm the earlier observations that cysts of Entamoeba histolytica offer greater resistance than any enteric

virus, including infectious hepatitis, to the disinfecting action of chlorine (Harvard Report, 1945). Morris (1966), for instance, quotes other investigators who state that the concentrations of HOCl needed to yield 99% germicidal effect in 10 minutes at 5°C for virus and cysts are 0.002-0.4 ppm and 10 ppm respectively. Chang (1966) presents data for iodine which shows that for a contact period of 10 minutes at 18°C and 99.9% kill, the concentrations of I_2 and HOI needed for poliovirus Type I and _E. histolytica_ are shown in Table 5.1.

TABLE 5.1

Species	Poliovirus Type I	_E. histolytica_
Iodine	20 mg/l	2.5 mg/l
Hypoiodous Acid	0.45 mg/l	4 mg/l

This data indicates that for effective disinfection of cysts and virus with reasonable doses of iodine, both molecular iodine and hypoiodous acid should be present in solution. It is interesting to note here that at pH 7, a dilute solution of iodine contains almost equal percentages of molecular iodine and hypoiodous acid (Black et al., 1965). This fact underscores the role the buffer has in a disinfecting tablet containing iodine.

5.4 Tablets in Use

There are currently two tablets being used for water disinfection in the U.S. The halazone tablet has been in use prior to

and during World War II. The disinfectant employed is a chlorine compound. The other tablet, globaline, which contains an iodine-based disinfectant, is used by the U.S. Armed Forces for the disinfection of canteen waters. This tablet was developed by the Harvard researchers and has many advantages over the halazone tablet for this purpose.

A. Standard Halazone Tablet - Composition and Reactions

The composition of this tablet is as follows:

Halazone - - - - - - - - - - - - -	= 5.30 mg
Soda Ash, dried - - - - - - - - - -	= 5.18 mg
Boric Acid - - - - - - - - - - -	= 11.92 mg
Sodium Chloride - - - - - - - - -	= 114.00 mg
Weight per Tablet - - - - - - - -	= 136.40 mg

The chemical name of halazone is p-dichlorosulfonami dobenzoic acid. It reacts with water to release hypochlorous acid up to 50% of the titrable chlorine present. One tablet dissolved in a quart of water produces a titrable chlorine* concentration of 2.3 ppm and a maximum concentration of HOCl (as Cl_2) of 1.1 ppm. The reaction of the halazone in water is as below:

$$Cl_2NO_2SC_6H_4COOH + H_2O \rightarrow Cl\ HNO_2SC_6H_4COOH + HOCl$$

* The Harvard researchers (Harvard Report, 1945) defined titrable chlorine as the total oxidizing power of the material or solution under consideration which is effective in oxidizing iodide ion to iodine in dilute acetic acid solution, expressed as ppm of elemental chlorine.

In this tablet sodium chloride is the filler and the remaining two compounds form an alkaline buffer.

B. Globaline Tablet - Composition and Reactions

The Globaline tablet derived its name from a chemical compound which was developed by the Harvard researchers. The Harvard Report (1945) refers to globaline as triglycine hydroperiodide, $(NH_2CH_2COOH)_3 \cdot HI \cdot I_2$. The formulation was later modified to tetraglycine hydroperiodide $(NH_2CH_2COOH)_4\ HI \cdot 1.24I_2$ (Summary Report, 1946). This compound provides 42.32% titrable iodine and 59.42% total iodine. The composition of the globaline tablet is as below:

tetraglycine hydroperiodide - - - -	= 19.3 to 21 mg
disodium dihydrogen pyrophosphate - ($Na_2H_2P_2O_7$)	= 82.5 to 92.3 mg
talc - - - - - - - - - - - - - - - - - -	= not more than 6 mg
weight per tablet - - - - - - - - - -	= 110 to 120 mg

One tablet dissolves in a quart of water to give 8 ppm of titrable iodine.

The talc is employed as a lubricant and disodium dihydrogen pyrophosphate works as an acid buffer as well as an excipient. This acid buffer serves to lower the pH of natural waters for it was then thought that elemental iodine was more germicidal in general than its main hydrolysis product, hypoiodous acid. As discussed earlier, Chang (1966) has shown that while molecular iodine is an excellent cysticidal agent, it has poor viricidal properties. On the other hand, hypoiodous acid requires about

double the dose of molecular iodine for killing cysts under the same conditions, but is about 40 times as viricidal as iodine. These results indicate the need for the presence of both I_2 and HOI in reasonable concentrations in water for effective disinfection of all organisms rapidly.

5.5 Comparison of the Two Tablets

The Harvard Report (1945) provides sufficient data on almost all properties of the two tablets discussed. The following is a summary of some of this data:

5.5.1 Dissolution Time

Field studies employing soldiers in acceptability tests indicated that they considered rapid solubility of tablet as a primary criterion for acceptability. They were impatient with agents that required a waiting period of more than 10 minutes.

For field simulation, the tablet to be tested was placed in a liter volumetric flask containing tap water at 23°C. The stoppered flask was then inverted end-over-end continuously, causing the tablet to drop through water until it was dissolved. These tests showed that while globaline disintegrated and dissolved in less than one minute, standard halazone tablets required 7½ minutes. Thus, in the case of halazone, the actual contact time between the disinfectant and the organism is 2½ minutes, if 10 minutes is taken as the total time a soldier will wait.

It may be mentioned here that the disintegration of the tablets is not primarily a function of the disinfecting agent but rather of the filler and expanding agent used in the tablet. Since

halazone contains sodium chloride which hardens or "sets up" with time, it suffers from a low rate of solution. As for the solubility of halazone itself, it was tested at different pH values. The results showed that the solubility was low and constant up to a pH of about 4. Above this pH, the solubility increased quite rapidly, either because of hydrolysis of the dichlor group or through ionization of the carboxylic acid group. For example, some values were as follows:

pH	3.8	5.5	5.6
halazone solubility, grams/liter	0.09	0.83	1.200

These figures indicate that a change in the filler now employed in Halazone might improve the dissolution time of the tablet markedly. On the other hand, the use of disodium dihydrogen pyrophosphate as a buffer and free-flowing filler in the globaline tablet was a marked improvement even though the solubility of globaline compound itself is far greater than that of halazone. Globaline has a solubility of 380 grams per liter of distilled water.

A. Effect of Storage and Humidity on Dissolution Time

In general tests showed that storage at 140°F and room humidity did not affect the dissolving properties of the tablets tested.

B. Effect of Temperature on Dissolution Time

In general, lowering of the water temperature increased the time of dissolution for both the tablets substantially in accordance with the Van't Hoff-Arrhenius formulation. Some of the dissolution

times obtained were:

	10°C	20°C	30°C
Globaline	1.9 min	1.2 min	0.8 min
Halazone	9.5 min	8 min	6.5 min

5.5.2 Cysticidal Dose

Cysticidal doses of globaline and halazone tablets were determined in Cambridge tap water alone or with the addition of interfering substances that might be present in natural polluted water. The cyst density was 60 per ml of water. This density is considered to be far higher than the highest conceivable concentration of cysts in sewage. This estimate is based on an area of high endemicity, say 50%, where the ratio of amoebic cysts to E. coli would be of the order of 1 to 100,000. (The number of coliform organisms discharged by an individual is estimated to be about 400 billion per day and an infected individual would discharge cysts in numbers varying from several hundred to some ten million per day.) This ratio would make the number of cysts in concentrated sewage about 10/ml.

The tests with globaline gave the following results:

TABLE 5.2

Kind of Water	Temp °C	Contact Time, Minutes	pH Initial	pH Final	Cystici-dal Dose Tablet/Qt.	Cysticidal Residual I_2-ppm
Tap	3	25	8.0 to 9.0	6.5	1	7.5
Tap	10	15	8.0 to 9.0	6.6	1	6.9
Tap	23	10	8.0 to 9.0	7.3	1	7.5
Tap	28	5	8.0 to 9.0	6.65	1	7.5
Tea Infusion	23	5	7.2	6.4	2	8.7

The above data certifies that one tablet of globaline should be able to disinfect all cysts, pathogenic bacteria and spores. No conclusive tests were carried out against organisms of infectious hepatitis and other enteroviruses. Nevertheless, it is possible now to estimate the viricidal capacity of waters disinfected with globaline. At 10°C, the initial pH of tap water was lowered to 6.6 with one globaline tablet thereby leaving a residual of 6.9 ppm of iodine. At pH 6.6, about 5% of the titrable iodine is in the form of HOI (Chang, 1958). As a result, the hypoiodous acid concentration is about 0.35 ppm. This amount of HOI may not be sufficient to be viricidal. The high concentration of titrable iodine and the use of an acidic buffer result, therefore, in a high cysticidal efficiency but lower viricidal capacity.

The tests with halazone tablets showed that at room temperature about 5 tablets per quart of water were required to destroy all cysts in 10 minutes, whereas 2½ tablets would do so in 30 minutes. In moderately to heavily polluted water at the same tempera-

ture, 7 tablets were needed for 10 minutes contact time and about 5 to do so in 30 minutes. Larger dosages of these tablets are required for the following reasons:

A. This tablet can release a maximum concentration of titrable chlorine equal to 2.5 ppm and HOCl equal to 1.25 ppm. This is far less than the dose required under adverse conditions. Morris (1966) reports that 10 ppm of HOCl are required for 99% kill of E. histolytica in 10 minutes at 5°C.

B. The halazone tablet has an alkaline buffer to aid in dissolving the compound. Unfortunately, at high pH the predominant species of chlorine is OCl^- which is about 100 times less cysticidal than HOCl.

C. The dissolution time of the halazone tablet is slow; 7½ minutes at room temperature. Halazone has a great advantage in that HOCl reportedly is an excellent viricidal agent (Morris, 1966; Kabler et al., 1961). It may be safe to assume, therefore, that if a certain dose of HOCl is cysticidal, it is also sufficient for all types of enterovirus. In summary, a major improvement which appears to be possible in the preparation of tablets containing halazone is the inclusion of an acidifying agent which will not affect the solubility of the compound.

5.5.3 Acceptability of Tablets by Users

The acceptance of the disinfecting agent by the user is probably as important as its germicidal action. The user may hesitate to use the agent because of (a) unpleasant taste, odor or color, (b) adverse physiological reaction, or (c) excessive time for disinfection.

A. Unpleasant Taste, Odor or Color

Tastes and odors may be caused either by the tablet itself in water or by its combination with beverage powders.

For purposes of comparison, the Whipple Scale of intensity of odors and tastes (Whipple, 1927) was adopted as a yardstick to determine the relative palatability of the tablets. Investigators (Harvard Report, 1945) used four tablets of halazone providing about 10 ppm of titrable chlorine and one tablet of globaline providing 8 ppm of titrable iodine per liter of boiled distilled water at 23°C. The pH was varied with citric acid, dihydrogen disodium pyrophosphate or sulfuric acid. The water was tested by seven to fourteen subjects. The results obtained indicate that in the "pH range commonly encountered," the globaline was more acceptable than halazone. In fact, in this range of pH, globaline produced "faint" to "distinct" intensity of odor and taste whereas halazone treated water had "decided" to "very strong" range on the Whipple scale.

The "objectionable thresholds" were also determined in boiled distilled water at 23°C and the results were as follows:

Compound	Percent of Normal Cysticidal Dose at which "Objectionable Threshold" is Reached					
pH	4	5	6	7	8	9
halazone	50	40	25	25	25	25
globaline	-	200	-	200	-	-

From this it is apparent that globaline would reach the "objectionable threshold" only if 2 tablets were used as is prescribed for heavily polluted waters.

As for the effect of pH upon tastes and odors, it was deduced, though not conclusively, that minimum tastes and odors were produced at the pH values attained when the tablets are added to neutral, unbuffered waters.

To study the effect of temperature on the tastes and odors, tests were made at temperatures of 15°C, 23°C, and 30°C. The results indicate that the intensity increased with temperature but did not become objectionable even at 30°C, although at that temperature no water is pleasant to drink. All observers agreed that the coldest drink was the most palatable.

With regard to the effect of disinfection on beverage powders, no specific tests were then made with either of the two tablets.*

B. Adverse Physiological Reaction

The physiological response of the use of iodinated water has long been a matter of concern. A number of laboratory as well as field studies have been reported. Studies were conducted at:

1. Department of Pharmacology, Harvard University (Dr. Otto Krayer)
2. Division of Pharmacology, Food and Drug Administration
3. Army Medical Research Laboratory, Fort Knox
4. Naval Installations, Marshall Islands

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* Hurst and Bird (1968) have now found, however, during their field tests with globaline that soft drink mixes are used in the field to make contaminated water more palatable.

All of these investigations were performed using iodine in concentrations equivalent to or in excess of those used in the field purification process. The tablets themselves were not used in these tests. The first three studies or their conclusions have been described in the Harvard Report (1945) whereas the fourth study has been reported by Morgan and Karpen (1953). While the first three studies indicate in general that the ingestion of iodine-disinfected water by healthy male adults should have no injurious effect, the analysis of data in the fourth study revealed no evidence of weight loss, failure of vision, cardiovascular damage, altered thyroid activity, anemia, bone marrow depression, renal irritation, sensitization to iodine, predisposition to diseases of the skin, or impaired wound healing.

A more exhaustive study is now underway at Gainesville, Florida, under Dr. A. P. Black where far lower dosages of iodine are being used. Partially reported results indicate that there is no evidence that iodine, under the experimental conditions employed, has had any detrimental effect on general health or thyroid function (Black et al., 1965; Black et al., 1968).*

C. Excessive Time of Disinfection

As reported earlier, the acceptability tests show that the soldiers in the field are impatient with disinfectants which take

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* Chang (1968), however, suggests that the tests should be extended to pregnant women, infants and small children to know their reaction to small amounts of iodination over a long period of time.

more than 10 minutes to complete their action. In other words, the dissolution should take place in a matter of seconds to leave about 10 minutes contact time for sterilization. Obviously halazone tablets which require more than 7 minutes for solution, have to compensate for a shortened contact time by higher dosage. Globaline, on the other hand, is reported to dissolve in less than a minute, thus leaving most of the 10 minute time for disinfection.

5.5.4 Thermal Stability of Tablets

Water disinfecting tablets designed for global use must be capable of withstanding extremes in air temperature as well as heat developed in storage warehouses. To test the stability of globaline, accelerated storage tests at 140°F and room humidity were carried out to determine the rate at which tablets decompose and at what rate active ingredients are dissipated.

Tests on globaline powder indicate that it lost about 30% of its iodine after one month and about 60% after two months. On the other hand, results of experiments with halazone tablets indicated that no appreciable loss of available chlorine occurred after 20 days at 140°F. Therefore, the halazone tablet can be described as thermally stable.

5.5.5 Resistance to Humidity

To determine the relative stability of tablets in humid atmospheres, they were subjected to tests at humidities of 100%, 79% and 55% at room temperature. The gain in weight after certain time intervals at room temperature was measured.

At 100% humidity globaline appeared to be more stable than halazone as the former retained 37% of original iodine and the latter 24.7% of original chlorine after the same number of days.

At 79% humidity as well as 55% humidity, globaline appeared to be less hygroscopic. Over long periods of time at 32% humidity, globaline again proved to be a stable substance.

5.5.6 Simulated Field Test

In order to gauge resistance to humidity and thermal stability during actual use in the field, bottles of globaline and halazone tablets, with and without cotton plugs, were placed in a control room held at 80 to 90% humidity and approximately 80°F. Every two hours during the day each bottle was opened for a minute and a tablet was drawn. Over a three-week period, none of the compounds showed an appreciable loss of strength, and there was little variation between the bottles with or without cotton plugs.

5.6 Corrosion of Metals

To see the effect of halazone and globaline disinfected waters on the materials of canteens, a series of experiments was conducted on aluminum and steel canteens. To perform accelerated tests, the strength of solutions was quadrupled. Thus, the globaline solution contained 32 ppm of titrable iodine and the halazone solution had 20 ppm of titrable chlorine. Two types of tests were conducted, drip tests and immersion tests.

5.6.1 Drip Tests

In the drip tests, the solutions were allowed to drop

upon the experimental metal and run down it for about 9 hours each day over a period of 36 to 50 days. The same solution was used over and over again, but it was freshly reconcentrated each day with the respective tablets. The loss in metal was assumed to be an indication of corrosion. The results showed that the steel canteen metal was much more resistant to corrosion than the aluminum metal. Upon aluminum, globaline appears to be more corrosive than halazone, although upon steel, the action of globaline is less pronounced than that of halazone.

5.6.2 Immersion Tests

In normal immersion tests with the same solutions of globaline and halazone tablets, the former was less corrosive than the latter on steel canteen but the reverse was true in case of aluminum canteens.

5.7 Conclusions

The globaline tablet was developed as a result of a tremendous effort on the part of scientists and engineers at Harvard. It has satisfied most of the criteria set for a disinfecting tablet. The halazone tablet suffers from serious drawbacks which limit its efficiency. However, since the production of these tablets, much work has been done on the subject of disinfection and many misconceptions have been corrected. It may be possible, therefore, to re-evaluate the potency of these products and make further improvements.

Globaline was produced on the basic assumption that molecular iodine alone is germicidal (and not its hydrolysis products) and

that cysts of E. hystolytica represent the test organism. Molecular iodine is still known to be an extremely good cysticidal agent but it has been proven by several researchers (Chang, 1966; Kabler, et al., 1961) that it is much less viricidal. The Harvard Report (1945) assumed that "the destruction of virus by disinfectants appear to be of the same order of magnitude as that of most pathogenic nonsporulating bacteria." Since this assumption has been disproven (Morris, 1966; Kabler et al., 1961) it would be useful to evaluate the viricidal power of globaline tablets. As discussed in paragraph 5.5.2, due to the effect of disodium dihydrogen pyrophosphate (acidic buffer) in lowering the pH of the water, the hypoiodous acid content produced of the water may be so low that it may be insufficient to kill any virus present. This situation points to an area of possible improvement in the globaline tablet. The substitution of an alkaline buffer (pH 8) would yield about 40% HOI and 60% molecular I_2.

At room temperature the globaline tablet was expected to dissolve in less than a minute. Studies at the University of Illinois (O'Connor, 1967) have indicated that it may take longer, perhaps from 3 to 4 minutes. However, this experimentation was done on tablets which had been manufactured a few years earlier. The discrepancy may be ascribed either to the adverse effect of storage on the solution properties of the tablet or the pressure exerted by tableting machines. Since these factors are difficult to control, further studies to find a more suitable swelling agent are indicated. An alternative would be an effort to make the tablet effervescent.

This problem is one that involves the psychology of the thirsty soldier and improvements towards a more satisfactory solution should be constantly pursued.

Color, taste and odor problems are associated with the use of globaline tablets but not to an extent that it is alarming. In fact, these signs are significant as they indicate the presence of a fair amount of residual iodine.

The halazone tablet, at present, is not a suitable disinfecting agent for military use. Not only because little titrable chlorine is released, but also because most of the chlorine released ionizes into OCl^- due to the presence of an alkaline buffer. Since OCl^- is about 100 times less cysticidal than HOCl, the efficiency of the chlorine is greatly reduced. The alkaline buffer was added to increase the rate of solution of halazone which is very low at low pH values but increases markedly above a pH of 6. It might be possible, therefore, to prepare a reasonably soluble tablet buffered at a pH of 6 rather than 8 or 9. The solubility might further be enhanced by the addition of a swelling agent or by making it an effervescent tablet.

Comparing iodine and chlorine based tablets as disinfectants for small water supplies, the former appears to have advantages over the latter for the following reasons:

1. On molar basis, iodine is more cysticidal than hypochlorous acid.
2. Iodine has very little organic demand as compared to chlorine.

3. Chlorine has a strong affinity for nitrogenous matter, whereas iodine has almost none.
4. Both predominant forms of iodine, molecular iodine and **hypoiodous** acid, are efficient germicides. They form an excellent combination for cysts and enterovirus. On the other hand, where chlorine is used, hypochlorous acid alone is a good germicide while OCl^- is a poor disinfectant.

Finally, the present practice of packaging 50 tablets of globaline in a single bottle may also be subject to improvement. Once opened for the use of first tablet, the remaining tablets may start to "set up" or harden. In addition, the disinfecting agent may be lost. With the tremendous improvements in packaging techniques and materials, it may not be difficult to devise a package which contains one or two tablets. Alternately, the use of a powder pillow may be a solution to the problems of stability and solubility.

Chapter 6

POINTS TO PONDER

6.1 Introduction

The following discussion is an attempt to prepare a list of some of the many problems facing disinfection of public water supplies which appear to be very urgent and need attention in the near future. It is the opinion of the writer that research on disinfection of water is in a period of comparative stagnation. This view is supported by an informal survey which shows that very few universities and government research institutions are conducting research on problems associated with water disinfection. In the private sector, the situation is even worse. The response of prominent chemical companies producing disinfecting chemicals to inquiries about new or improved disinfectants for water was negative. This may be regarded, within limitations, as a reflection on the feeling prevalent in the water works industry that all disinfection problems are solved.

6.2 Biological Standards for Potable Water

The USPHS (1962) standards for the biological quality of drinking water are based on a limitation of the numbers of the coliform group in water. A question exists as to whether or not these limits ensure the absence of water-borne pathogenic virus in addition to other pathogens. The numbers of virus in water supplies is believed to be increasing due to continued low level transmission of viral infection in many communities in spite of adherance to the established standards. Mosley (1965) comments that "we must consider, therefore,

the possibility that present standards of water treatment are not adequate to prevent low levels of virus from intermittently producing what appear to be sporadic cases of infectious hepatitis and other viral diseases." Chang (1968) endorses Mosley's idea and suggests the establishment of an entero-virus index which is, of course, beyond reach until a reliable virus detection method is standardized. Until such a time, Chang suggests two procedures to be followed separately or in combination:

1. "If polluted water is used as a source and if cases of enteric viral diseases, i.e. infectious hepatitis, occur without a known mode of transmission, ... steps should be taken to ensure the safety of the finished water." (Chang, 1968).
2. A tentative enterovirus index should be established for communities where virological services are available, where with the help of presently known methods of detection and quantification (Chang, 1968) monitoring may be practiced. This will involve establishing enterovirus coliform group ratios in the water and might indicate the necessity for an upward revision of existing water supply standards.

Morris (1966) suggests that "some better index than the number of coliform organisms must be found for the assessment of the hygienic quality of treated water supplies." As an interim solution, he suggests the revival of the old total plate count at 20°C which should indicate the presence of some sporulating organisms which are even more resistant to chlorination than viruses. An appropriate

decrease in their number might well serve as an indicator of viricidal activity.

The importance of viral challenge can be estimated from Berg's (1966) speculation that some viruses, when infecting unnatural hosts, may produce cancers in these hosts. He maintains that there is no proof available that viruses of other than human origin cannot enter and infect human cells.

6.3 Disinfection Capacity

As discussed in earlier chapters, the terms "residual free chlorine" and "residual combined chlorine" do not provide a clear picture of the disinfecting capacity of the aqueous solutions unless they are properly interpreted by subsequent calculation. Any attempt to replace these terms may have to wait for new analytical techniques which directly measure concentrations of each individual species present in the solution. The same is true for iodine and bromine solutions.

The misleading nature of these terms in waterworks practice needs to be corrected meanwhile. An interim solution to the problem is the provision of tables or nomograms or even specially designed slide rules for the operator, which would calculate the actual "disinfecting capacity" of the water once he determines the analytical values of the above, pH, the concentration of ammonia-nitrogen and temperature. The "disinfecting capacity" of the water may be defined as below:

$$\text{Disinfecting capacity} = D_1 \times r_1 + D_2 \times r_2 + D_3 \times r_3 \ldots$$

where D_1, D_2, D_3, . . . are the concentrations of the

various species and r_1, r_2, r_3 . . . are the germicidal efficiencies of corresponding chemical species for a particular contact time and temperature. Of course, the disinfecting capacity of the solution will be different for each specie of organism. This procedure can be used either to calculate the dosage required for a particular percentage kill or to check the residual active disinfectant.

Chang and Morris (Personal Communications 1, 2) appeared to be in favor of such a method.

6.4 Analytical Techniques

The analytical techniques for the various forms of chlorine have not changed markedly in over a quarter of a century when the distinction between "free available chlorine" and "combined available chlorine" was first demonstrated analytically. Since then a breakthrough in differentiating between the various species present in the aqueous solutions of chlorine has been anticipated by those in the waterworks profession. A search of the literature indicates that no serious effort is being made in that direction.

Chang (Personal Communication - 1) suggests studies on the role of redox potential as a possible measure of various species while Morris (Personal Communication - 2) proposed the use of membranes which permit ions (OCl^- for example) to pass through while molecular form ($HOCl$) is retained. Obviously intensive efforts are needed to break the existing stalemate.

6.5 Mechanism of Devitalization

Another yet unresolved question in our study of disinfection is the mechanism behind the devitalization of various organisms by different disinfecting agents and their associated species. Much progress has been made in this area since the review of prevailing theories was set forth by Chang (1944). His own specific investigations on Endamoeba histolytica with chlorine and its various compounds led him to state that "although both oxidation of the proteins in the protoplasm and chlorination of the proteins to form chloramine may occur when the penetrating chlorine is in contact with the protoplasm, the destructive changes taking place probably render the cyst non-viable long before the newly formed chloramine has a chance to poison the cyst."

In their classic review of the disinfection in general and mechanism of cell destruction in particular, Fair et al. (1948) held that the ability of the reagent to react with the enzyme system of the organism and its capability to gain access to the enzyme by penetrating through the cell wall was responsible for devitalizing the contact cell. They also thought that the rate of diffusion of the active cell through the cell wall would "largely determine the rate of disinfection and relative efficiency of various disinfecting materials." Based on this hypothesis, they listed oxidizing power, molecular size and electrical neutrality the determining factors in this regard.

Knox, et al. (1948) also pointed out that bacterial spores may be killed by a mechanism that is entirely different from vegetative cells.

Berg, et al. (1964) reported on their experiments with iodine and virus and suggested that the devitalization of the virus results from the interaction of a single molecule of I_2 with a single vital site on the virus. They felt that the greater sensitivity of bacteria may be attributed to the greater number of vital sites present in these larger organisms. Regarding the greater resistance of spores and cysts, they relate the slow diffusion of I_2 through the walls of the organisms, resulting in lower effective concentrations in the areas where devitalization takes place. They presume that "stripped of the protective coats, spores would be as sensitive as their vegetative forms, and the large cysts even more so."

Benarde, et al. (1967) experimented on the bacterial disinfection with chlorine dioxide and were of the view that the mechanism of chlorine dioxide will occur via disruption of protein synthesis.

Chang (1966) analyzes the different disinfecting powers of I_2 and HOI against spores, cysts, virus and vegetative bacteria on the basis of existing data and states that "when the disinfection process is directed against microbes that are protected by a resistant cell or spore wall, the superiority of I_2 over HOI apparently is because of the greater penetrating power of I_2. In the killing of microbes with a physiologically active cell-membrane, as in the case of vegetable bacteria, the oxidizing power of the compound becomes more important." He also supported the belief that virus destruction is a result of the reaction of the agent with the protein shell and not the nucleic acid core.

Thus, although the various opinions on the phenomena are in a converging trend, the final explanations will be very much dependent on what further knowledge is gained in the field of microbiology in general and virology in particular.

6.6 Search for an Ideal Disinfectant

In the years to come the quality of the water available at water treatment plants may be much worse than it is at present. This is suggested by the estimates made by Berger (1968) in that the total reuse of water in the U. S. may increase from about 10 bgd in 1960 to about 100 bgd in 1980. This is about 16% of the total fresh water requirements in 1980. At the same time, according to estimates of the Senate Select Committee on Water Resources (1960), the number of persons served by the municipal water supply systems in 1980 is expected to be 70% greater than in 1954. Thus, with decreasing quality and increasing quantity requirements, more attention must be given to water disinfection. Moss (1967) writes in his preface to "The Water Crisis" that "for the next generation of Americans, I believe it is not an exaggeration to say that water - its competing uses and the conflicts that arise out of those uses - may be the most critical natural problem." It is realized that his concern here is for the water resources in the nation as a whole but the drinking water is of no small importance.

The role of the disinfection in the future is obvious. Merely increasing the production of chlorine, in particular and disinfectants, in general, will not solve our problems. A more rational attitude should be developed toward disinfection and scientific

efforts should be intensified to obtain disinfectants which are functional over the range of conditions encountered in water treatment and which are economical at the same time. With more stringent standards of acceptability, our search for an ideal disinfectant must continue.

APPENDIX

DEFINITION OF TERM "WATER-BORNE"

The definition of the term "water-borne" has always been a matter of controversy. In an effort to resolve this situation, Mosley (1965) has tried to make it more broad-based. His approach is as follows:

1. "An agent may be considered as <u>frequently</u> water-borne if elimination of this route causes a significant reduction in the total incidence of the disease it produces." To place an agent at this level of occurrence indicates that control of waterquality plays an important part in control of the disease.
2. An infectious agent would be considered only <u>occasionally</u> water-borne if elimination of water as a vehicle made no appreciable difference in the total amount of disease, other than in limited areas for limited periods of time. The possibility of water-borne transmission, however, would require serious consideration in any epidemiological investigation. It would also be necessary to maintain water quality standards which would prevent supplies from serving as a vehicle for such agents, even though these standards would not contribute to overall control.
3. Finally, an infectious agent would be defined as <u>rarely</u> water-borne if few episodes were found, especially if these occurrences were the result of proximate contamination or unusual circumstances.

[illegible]

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JNEWWA:	Journal New England Water Works Association
P.H. Reports:	Public Health Reports
W.P.C.F.:	Water Pollution Control Federation

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